^{13}C NMR Investigation of the Size of the Moving Units in Polybutadienes of Various Microstructures

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Introduction

The characterization of the segmental motions of a polymer chain either in solution or in the melt is routinely obtained in terms of correlation times and activation energies from a number of spectroscopic techniques such as NMR, dielectric relaxation, ESR, or fluorescence depolarization. However, a comprehensive description of the segmental motions requires the determination of the geometry of the motions, the size of the moving units, or the length of cooperativity. Computer simulations based on Brownian dynamics,[1,2] molecular dynamics,[3] or the cooperative kinematics approach[4,5] have shown that the conformational jump of a given bond is accompanied by the reorientation of a very limited number of neighboring carbons. Experimentally, the extent of the moving unit has been estimated in an indirect way by following the behavior of fluorescence probes of different sizes diluted in the polymeric matrix. The moving unit is on the order of three monomer units in bulk *cis*-1,4-polyisoprene at temperatures far above the glass transition temperature.[6] However, until now, no direct experimental evidence of this result has been obtained.

Among the various techniques that permit the investigation of local dynamics, ^{13}C NMR spin−lattice relaxation is a very powerful tool. The main advantage of ^{13}C NMR is its high resolution. In atactic polymers and in copolymers, ^{13}C carbons belonging to different sequences often show distinct resonances. For example, the solution ^{13}C NMR spectra of polybutadienes containing cis-1,4, trans-1,4, and vinyl-1,2 units exhibit well-resolved olefinic and methylene lines in terms of three-unit sequences[7−9] which permit the determination of the ^{13}C spin−lattice relaxation time, T_1, of the olefinic and methylene carbons in each triad.[8,10] Therefore, polybutadienes of varying microstructure are of particular interest for studying how the motion of a well-defined sequence of three monomer units (which can be investigated by ^{13}C NMR) depends on both the chemical structure of these three units and the composition of the copolymer.

The purpose of the present paper is to take advantage of the sensitivity of local dynamics to microstructure and composition to derive information on the size of the moving unit in polybutadienes in solution. The technique used will be the determination of ^{13}C NMR spin−lattice relaxation times, T_1. In the absence of specific polymer−solvent interactions which may favor other relaxation mechanisms,[11] the dipolar mechanism of ^{13}C spin−lattice relaxation in polymers has long been established.[12] In *cis*-1,4-polybutadiene,[13] as well as in a number of other polymer systems[14−16] either in solution or in bulk at temperatures well above the glass transition temperature, the detailed analysis of a large number of relaxation data has shown that the local motions observed by ^{13}C spin−lattice relaxation can be satisfyingly described in terms of a damped diffusion of bond orientation along the chain sequence, which represents the segmental motions, and independent bond librations.[14] However, as shown by the expression of the orientation autocorrelation function in ref 14, segmental motions and librations contribute to the relaxation in a complex way. Therefore, the direct comparison of the segmental mobility of different carbons inside the same chain is not straightforward. For example, in *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene, the T_1s of the olefinic and methylene carbons, which share the same local segmental dynamics, are not in a ratio of 2,[10] as expected from the number of protons directly bound to the carbon of interest. Such a result is due to the librations of the C−H vectors, the amplitude of which depends on the steric hindrance at the site of the considered carbon.[13] In the following, since we are interested in the qualitative variations of the segmental dynamics only, we will compare T_1 data obtained for carbons that have the same libration amplitude, for example, T_1 data for a carbon of a given well-defined sequence of three monomer units as a function of the polybutadiene composition or T_1 values obtained for methylene carbons of cis-1,4 and trans-1,4 units that have been shown to have the same libration amplitude.[17] Moreover, we will consider only results obtained on the methylene carbons, which all reflect the local dynamics of the main chain, whatever the unit to which they belong, whereas olefinic carbons are either located on the main chain (1,4 units) or side chain (1,2 units).

Table 1. Code Names, Microstructures, and Glass Transition Temperatures, T_g, of the Samples Investigated[a]

code name	% vinyl-1,2	% cis	% trans	T_g (°C)
PB12	13	37	50	−90
	11	38	51	
PB24	24	38	38	−83
	22	35	43	
PB33	33	27	40	−75
	31	30	39	
PB54	54	21	24	−59
	55	18	27	
PB76	76	10	14	−32
	76	11	13	

[a] For each sample, the first line indicates the result of the composition determination as obtained from infrared spectroscopy, whereas the second line lists the ^{13}C NMR data.

Experimental Section

The polybutadiene samples were kindly supplied by Michelin. They were prepared by anionic polymerization, which is known to yield a random distribution of the three units.[8] Their microstructure was determined by IR spectroscopy and ^{13}C NMR, using either the olefinic resonances according to ref 7 or the aliphatic lines according to refs 8 and 9, which did not result in significant differences. IR and NMR values derived for the cis-1,4, trans-1,4, and vinyl-1,2 unit contents are shown in Table 1, together with the code names of the polymers. Results obtained from the two techniques are in satisfying agreement. The ratios of the number of cis to trans units, which lie in the range from 1.1 to 1.4, are of the same order of magnitude in all the samples. Thus the number of vinyl-1,2 units is the main variable in the series of samples investigated. No evidence of head-to-head or tail-to-tail additions, with characteristic resonances around 49, and 32 and 44 ppm, respectively, has been observed.[8]

The solvent used was $CDCl_3$. The polymer concentration was 0.1 g cm^{-3}. ^{13}C NMR spectra at 25.18 MHz were recorded at 300 K on a Bruker AC-100 spectrometer, using proton noise decoupling. ^{13}C chemical shifts were determined from $CDCl_3$

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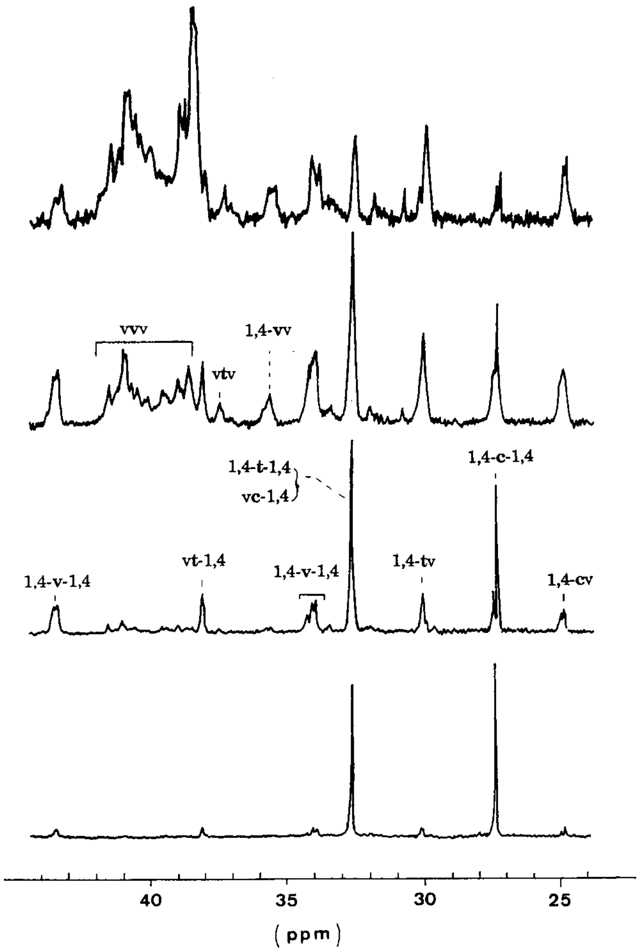

Figure 1. ^{13}C NMR spectra of the aliphatic carbons of PB12, PB33, PB54, and PB76 (from bottom to top).

as an internal reference (δ = 77.0 ppm). ^{13}C spin−lattice relaxation times, T_1, were measured using the standard (180°−τ−90°) inversion recovery pulse sequence, with a 10 μs 90° pulse duration and repetition times between pulse sequences >5 times the longest T_1 of the considered nuclei. The accuracy for each T_1 measurement is on the order of ±0.05 s. Distorsionless enhancement of polarization transfer (DEPT) experiments, using a proton 90° pulse length of 20 μs, were performed to discriminate the CH and CH$_2$ groups in the aliphatic region.

In the following, cis-1,4, trans-1,4, and vinyl-1,2 units will be represented by c, t, and v, respectively. The unit in a sequence that is responsible for the observed resonance will be written in bold.

Results and Discussion

Figure 1 shows the NMR spectra of the aliphatic carbons of polybutadiene in order of increasing content of vinyl-1,2 units. The resonance assignments were made in terms of triads according to the results of Sato *et al.*[8] and Wang *et al.*[9] They are summarized in Table 2. Polybutadienes which are predominantly of 1,4 microstructure show two major signals at 27.3 and 32.6 ppm, corresponding to **c** and **t** methylene carbons next to a 1,4 unit, respectively. Methylene carbons in 1,4 units next to a 1,2 unit (1,4−**c**v and v**c**-1,4, 1,4-**t**v and v**t**-1,4) are shifted toward either smaller or higher chemical shifts, depending on whether the methylene considered is closest to the vinyl-1,2 or to the 1,4 group.[8] Resonances of vinyl-1,2 units have a great variability because of the tacticity of 1,2 sequences. DEPT experiments show three regions for the methine group of the vinyl unit: 38.6−39 ppm for v**v**v triads, 41−41.6 ppm for 1,4-**v**v and v**v**-1,4 triads, and 43.4−43.6 ppm for 1,4-**v**-1,4 triads. Methylene carbon resonances occur at around 34 ppm for 1,4-**v**-1,4 triads and overlap methine signals in the 35.5−40.7 ppm region for other triads. At high vinyl contents (PB54, PB76), a methine carbon line at 30.9 ppm has not been assigned.

T_1 values measured at 25 MHz and room temperature are reported in Table 2 for the different triads of the aliphatic region. For PB54, our results are close to those determined by Sato *et al.*[8] at 50 MHz and 35 °C on a polybutadiene of similar microstructure (57% vinyl-1,2, 18% cis-1,4, 25% trans-1,4). The only difference between the two data sets concerns the aliphatic methylene carbons of 1,2 units in the 39−40.7 ppm region, for which Sato *et al.* measured a larger T_1.[8] This discrepancy may originate from the resonance dispersion that results in a low signal-to-noise ratio and from the overlap of methine and methylene signals which is larger at 25 MHz than at 50 MHz.

The relatively high values determined for T_1 at 25 MHz indicate that all T_1 are in the extreme narrowing regime or not far from this regime. Therefore, for carbons that exhibit identical librations, an increase in T_1 is indicative of an increase in mobility. As shown by results displayed in Table 2, at a given composition, each sequence of three units has a specific behavior. Although the lines from the 1,4-**t**-1,4 and v**c**-1,4 carbons overlap at 32.6 ppm, T_1 values obtained for PB12, in which the vc-1,4 content is very low, show that the mobility of a cis unit in a 1,4 environment (T_1 = 1.10 s) is higher than the mobility of a trans unit in the same environment (T_1 = 0.80 s). In trans-1,4 units, the shortest T_1s are observed when both neighbors are vinyl-1,2 units, as shown by the results listed in Table 2 for the v**t**v carbons in PB54 (T_1 = 0.31 s) and PB76 (T_1 = 0.22 s).

For the purpose of our study, it is of interest to compare the behavior of the 1,4-**t**v (or v**t**-1,4) and 1,4-**t**-1,4 sequences which have two common units and differ only by the nature of the third unit. The T_1s of the central trans carbons of the 1,4-**t**v and v**t**-1,4 sequences are equal within experimental error. They are shorter than the T_1 of the corresponding carbon of the 1,4-**t**-1,4 sequence in PB12, where the amount of vinyl-1,2 units is small enough so that the contribution of the v**c**-1,4 peak to the relaxation of the 32.6 ppm line can be neglected. These results imply that the moving segment involves three monomer units at least.

Figure 2 shows the variations of the T_1 values obtained for several triads, containing two 1,4 units at least, as a function of the 1,4-unit fraction, x. Whatever the triad considered, at low 1,4-unit fractions, T_1 is an increasing function of x. Then, when x is equal to 0.67 (PB33), T_1 reaches a plateau and does not undergo any further variation from x = 0.67 to x = 0.87 (PB12). These results can be interpreted in the following way: as previously observed by Gronski *et al.*,[10] the vinyl-1,2 units can be viewed as defects which are randomly distributed along the chain[7] and slow down the segmental mobility of the 1,4 units. When the relative amount of vinyl-1,2 units is large, that is for low values of x, the T_1 values of the triads considered in Figure 2 are short, indicating that the segmental mobility of the 1,4 units is considerably reduced due to the presence of a high number of vinyl-1,2 defects. The T_1 increase at small x values reflects the increasing mobility of the triads, based on two 1,4 units at least, as a function of the decreasing content of vinyl-1,2 defects. In contrast,

Table 2. Chemical Shift Assignment of the Aliphatic Region in Polybutadienes of Different Microstructures and Relaxation Times (in s) of the Corresponding Carbons

δ (ppm)	assignment	PB12	PB24	PB33	PB54	PB76
24.9	1,4-**c**v	0.67	0.75	0.75	0.55	0.39
27.3	1,4-**c**-1,4	1.10	1.10	1.16	0.92	0.70
30.0	1,4-**t**v	0.57	0.58	0.61	0.46	0.34
32.6	1,4-**t**-1,4 + v**c**-1,4	0.80	0.80	0.83	0.66	0.56
33.9−34.2	1,4-**v**-1,4 CH$_2$	0.56−0.59	0.55−0.62	0.61−0.67	0.46	0.33
35.6	1,4-**v**v CH$_2$				0.44	
37.4	v**t**v				0.31	0.22
38.1	v**t**-1,4	0.62	0.55	0.58	0.47	0.36
38.6	v**v**v CH				0.41	0.33
39.0					0.33	0.28
43.4	1,4-**v**-1,4 CH	1.05	1.03	1.10	0.87	0.83

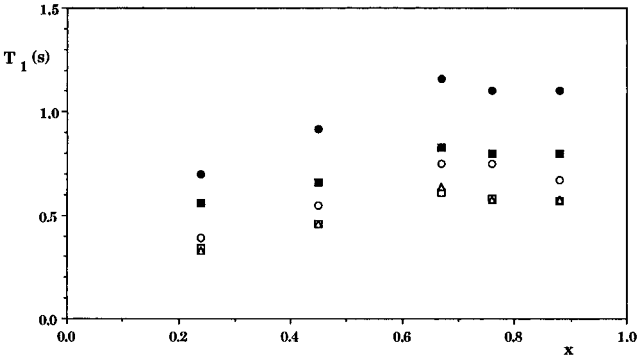

Figure 2. T_1 variations as a function of the 1,4-unit fraction, x: ○, 1,4-**c**v sequence; ●, 1,4-**c**-1,4 sequence; □, 1,4-**t**v sequence; ■, 1,4-**t**-1,4 + v**c**-1,4 sequences; △, 1,4-**v**-1,4 sequence.

when the relative amount of vinyl-1,2 units is small, that is when x is close to 1, the T_1 values are high and the segmental mobility of the 1,4 units is no longer affected by the presence of the vinyl-1,2 defects. Between these two regions, corresponding to small and large values of x, a plateau is expected to occur when the size of the moving sequence corresponding to elementary motions of the 1,4 units is on the same order of magnitude as, or is smaller than, the statistical repeat unit. In such a situation, the number of vinyl-1,2 units is statistically too low to modify the segmental dynamics of the 1,4 units in a significant way. Therefore, the absence of change in T_1 values observed in Figure 2 in the range from $x = 0.67$ to $x = 0.87$ can be interpreted in terms of a moving sequence, the size of which is comparable to the size of the statistical repeat sequence at the onset of the plateau (PB33), that is, three monomer units (two 1,4 and one vinyl-1,2 units). This result is in very good agreement with conclusions derived from computer simulations based on molecular dynamics[3] or on the cooperative kinematics approach[18] on polyisoprene and polybutadiene.

As shown in Figure 2, the T_1 variations are independent of the nature of the triad. This result suggests that the elementary motions which give rise to the segmental dynamics of the chain are largely correlated, the motion of a given elementary moving sequence inducing a cooperative transition of one of its neighboring bonds. This interpretation is in very good agreement with observations derived from Brownian and molecular dynamics simulations on *cis*-1,4- and *trans*-1,4-polybutadienes[19] and polyisoprene[3,20] which have detected a considerable degree of correlation in the conformational transitions of these polymers. It is also consistent with the physical description associated with the Hall−Helfand[21] and Dejean−Lauprêtre−Monnerie[14] orientation autocorrelation functions that are based on a damped diffusion of bond orientation along the chain sequence. In the polybutadienes under study, such a diffusion would control the spin−lattice relaxation of the different units of the chain, with an efficiency which depends on the frequency and/or amplitude of the elementary moving unit considered.

It is also of interest to relate the T_1 decrease observed in PB54 and PB76 to their unit distribution. Though the T_1s do not vary from PB12 to PB33, whatever the triad, the probability for a given monomer unit to have an adjacent vinyl-1,2 unit varies significantly from PB12 to PB33. Assuming Bernouilli statistics, which has proven to be a reasonable assumption in anionically prepared polybutadienes,[7] the probabilities of 1,4-1,4 and 1,4-v (or v-1,4) sequences also vary significantly, from 77 to 45% and from 20 to 44%, respectively. Only the vv probability has a weak dependence, from 1 to 11%, in this composition range and increases to 30 and 58% in PB54 and PB76, respectively. It is interesting to notice that the sudden T_1 decrease observed for each sequence at low 1,4-unit fraction and the increase in the number of vv sequences occur simultaneously. This result tends to indicate that the dynamics of the polybutadiene chain is strongly reduced by the presence of vv sequences.

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